

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 January 2001 (18.01.2001)

PCT

(10) International Publication Number
WO 01/04200 A1

- (51) International Patent Classification⁷: C08K 5/14, (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).
- (21) International Application Number: PCT/EP00/06246
- (22) International Filing Date: 3 July 2000 (03.07.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
11/192632 7 July 1999 (07.07.1999) JP
- (71) Applicants (*for all designated States except US*): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). KAYAKU AKZO CORPORATION [JP/JP]; Kojimachi NK Building, 14-2, Kojimachi, 2-chome, Chiyoda-ku, Tokyo 102 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): ISHIDO, Akio [JP/JP]; 7-6 Minatomati, Onoda-shi, Yamaguchi-ken (JP). TAKAI, Akihiko [JP/JP]; 1401-10 Oazanishikiha, Ube-shi, Yamaguchi-ken (JP).
- (81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/04200 A1

(54) Title: HIGH-CONCENTRATION CROSS-LINKING MASTERBATCHES

(57) Abstract: The invention relates to a cross-linking masterbatch comprising more than 40 % by weight of organic peroxide, a synthetic rubber, and a specific silica. More specifically, a highly concentrated cross-linking masterbatch is provided comprising from 40 to 70 % organic peroxide, a synthetic rubber such as EPM and/or EPDM, preferably having a propylene content of 45 % or more and a Mooney viscosity at 100 °C of 30 or more, and a wet-treated and/or dry-treated silica having a specific surface area of 150 m²/g or more or a porous silica having a pore volume of 1.4 ml/g or more.

HIGH-CONCENTRATION CROSS-LINKING MASTERBATCHES

- 5 The present invention relates to cross-linking masterbatches, more particularly to masterbatches to be used for the cross-linking of (elastomeric) thermoplastics and rubbers.

Thermoplastics, elastomeric thermoplastics, and rubbers, elastomers for short, 10 include preferred products such as polyethylene, ethylene-vinyl acetate copolymer, ethylene-propylene copolymer (EPM), ethylene-octene copolymer (POE), ethylene-propylene diene rubber (EPDM), and butadiene-acrylonitrile copolymer, all of which are low-priced, widely available, and have excellent physical properties that allow wide-ranging use. The elastomers can be cross-linked in a conventional way by heating in the presence of an appropriate 15 organic peroxide, e.g., to increase their heat resistance.

When cross-linking elastomers, it is preferred, from an economic point of view, to mix pure organic peroxide with the elastomer. However, such a procedure 20 often is not feasible in view of safety considerations. Also, it is known that the use of such pure organic peroxide leads to a less homogeneous distribution in the elastomer to be cross-linked, resulting in an unevenly cross-linked product with inferior properties, especially compared to a process where the elastomers are mixed with organic peroxides formulated with inactive fillers such as calcium 25 carbonate, silica, clay, and talc, or with a polymer or elastomer (so-called masterbatches), in the form of sheets or granules. Therefore, in industry generally powdery formulations and masterbatches in the form of sheets or granules are used.

- 30 Powdery formulations where the organic peroxide is diluted with inactive fillers have the following advantages when used as a cross-linking agent:
- (1) they are safe to store and handle,

- (2) because they are powders, they can be metered into the elastomer in a simple manner, irrespective of the organic peroxide (solid or liquid) used, and
- (3) they are inexpensive.

5

However, these powdery formulations suffer from the following disadvantages:

- (1) It typically takes too long to obtain a homogenous dispersion of the peroxide in the elastomers to be cross-linked,
- (2) the formulations tend to be dusting, leading to exposure of operators to dust during the metering of the formulation and while it is being kneaded with the elastomers to be cross-linked.

Masterbatches in the sheet or granular form, where the peroxide is dispersed in a polymer, preferably an elastomer, have the same benefits as powdery formulations. Additionally, they require less time to prepare homogeneous dispersions of the peroxide in the elastomer to be cross-linked and can be handled without dust being formed. Therefore, such (sheet or granular-type) masterbatches often are the product of choice for processes where a peroxide and an elastomer are to be intimately mixed.

20

However, sheet or granular-type masterbatches typically suffer from the fact that highly concentrated products cannot be formed. Where commercial powdery formulations are known to contain 50% by weight of peroxide, commercial sheet or granular-type masterbatches are limited to formulations containing 40% by weight of peroxide.

Conventional cross-linking masterbatches containing up to 40% by weight of organic peroxide, EPM or EPDM, and wet-treated or dry-treated silica as essential ingredients are known to be produced in a conventional way, e.g., on an open roll mixer, by kneading said ingredients, optionally with inactive fillers such as calcium carbonate added. The physical state of the organic peroxide, the properties of the EPM or EPDM (such as Mooney viscosity, ethylene or

3.

propylene content), and the properties of the wet- or dry-treated silica (such as specific surface area and oil absorption capacity) are not important in such a case. The wet- or dry-treated silicas used for this purpose have a specific surface area of 40-140 m²/g and a pore volume of 0.1-0.6 ml/g.

5

- However, if a masterbatch containing more than 40% by weight of a liquid organic peroxide is to be produced by kneading said peroxide with EPM or EPDM and such conventional dry- or wet-treated silica on a roll mill, the masterbatch tends to stick to the roll, making mixing more difficult, is difficult to remove from the roll in (thin) sheets, and results in sheets of inferior strength. Furthermore, it was found that the resulting sheets or granules are not storage stable. More specifically, they suffer from exudation of the peroxide from the masterbatch.
- 10
- 15 Similarly, if the masterbatch contains more than 40% by weight of solid organic peroxide, the mass on the rolls easily breaks up on the roll during kneading, making it difficult to knead the product efficiently. The resulting masterbatch was found to suffer from blooming of the peroxide from the masterbatch.
- 20 To overcome these problems, W098/54249 discloses the production process of a high concentration masterbatch which essentially contains liquid polymers such as EPM/EPDM having Brookfield viscosity at 60°C of 10,000 mPas and lower. However, these liquid polymers are expensive, which is considered to be the main reason why they have not gained wide market acceptance.

25

- Accordingly, there is still a need for peroxide masterbatches, especially EPM and/or EPDM based masterbatches, containing more than 40% by weight of either liquid or solid peroxide that do not dust, are easy to handle and storage stable, do not contain expensive low-molecular weight polymers, and lead to a homogeneous distribution in the elastomer to be cross-linked.
- 30

The high-concentration cross-linking masterbatches of the present invention

were found to solve these problems. They are characterized in that they contain a solid synthetic rubber, such as EPM and/or EPDM, as the base polymer, from 40 to 70% by weight of an organic peroxide, and a specific silica. More preferably, the masterbatches of the invention contain from 40 to 70% by 5 weight of organic peroxide and an EPM and/or EPDM rubber of which the propylene content is 35% by weight or more, preferably 40% by weight or more, more preferably at least 45% by weight, and a Mooney viscosity, determined from the ML 1+4 at 100°C, as is conventional in the art, of 30 or more. The specific silica that is to be used can be characterized by (a) its specific surface 10 area of at least 150 m²/g if the organic peroxide is solid at ambient temperature, or (b) its pore volume of at least 1.4 ml/g, preferably 1.5 ml/g or more, if the organic peroxide is a liquid at ambient temperature.

Accordingly, the present invention relates to:

- 15 (1) A cross-linking masterbatch containing at least one organic peroxide in an amount of from 40 to 70 % by weight, based on the weight of the total masterbatch, at least one synthetic rubber, and a silica having a specific surface area of 150 m²/g or more or a pore volume of 1.4 ml/g or more.
- (2) A high-concentration cross-linking masterbatch according to (1) above, 20 wherein said masterbatch contains the dry-treated or wet-treated silica with (a) a specific surface area of 150 m²/g or more if said organic peroxide is solid at ambient temperature, or (b) a pore volume of 1.4 ml/g or more if said organic peroxide is liquid at ambient temperature.
- (3) A high-concentration cross-linking masterbatch according to (1) or (2) above, wherein said synthetic rubber is an ethylene-propylene rubber or 25 an ethylene-propylene-diene rubber of which the propylene content is 45% or more and the Mooney viscosity at 100°C is 30 or more.
- (4) A high-concentration cross-linking masterbatch according to (1) to (3) above, wherein said organic peroxide is present in an amount of from 40 to 65% by weight, said synthetic rubber is present in an amount of from 30 to 30% by weight, and said silica is present in an amount of from 5 to 30% by weight, each based on the weight of the total masterbatch.

- Preferred organic peroxides for use in the present invention have a 10 hr half-life temperature of 60°C or more and are liquid or solid at ambient temperature. Ambient temperature here means about 15°C-30°C, depending on the region, 5 season, and working environment. The term "10 hr half-life temperature" is used in the conventional way, meaning the temperature at which 50% of the peroxide decomposes in 10 hours time when measured by thermal decomposition of a 0.2 mol/l solution of the peroxide in monochlorobenzene.
- 10 Preferred organic peroxides that are solid at ambient temperature include dialkyl peroxides, such as dicumyl peroxide, 1,3-bis(tert-butylperoxyisopropyl) benzene, and 1,4-bis (tert-butylperoxyisopropyl)benzene, and diacyl peroxides such as dibenzoyl peroxide.
- 15 Preferred organic peroxides that are liquid at ambient temperature include dialkyl peroxides, such as 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, tert-butyl cumyl peroxide, di-tert-butyl peroxide, and di-tert-amyl peroxide; peroxyketals such as 1,1-di-tert-butylperoxy-3,3,5-trimethyl cyclohexane, 4,4-di-tert-butylperoxy valeric acid n-20 butyl ester, and 1,1-di-tert-butylperoxy cyclohexane.

Of these organic peroxides, the more preferred ones for use in the master-batches according to the invention include dicumyl peroxide, 1,3-bis(tert-butylperoxyisopropyl) benzene, and 1,4-bis (tert-butylperoxyisopropyl) benzene, 25 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane, 1,1-di-tert-butylperoxy-3,3,5-trimethyl cyclohexane, and 4,4-di-tert-butylperoxy valeric acid n-butyl ester.

The organic peroxides can be used individually or as a mixture of one or more peroxides. A mixture can be handled either as a liquid or as a solid, depending 30 on its physical form at ambient temperature. The cross-linking masterbatch of the present invention may contain any of these organic peroxides in a total peroxide concentration of from 40 to 70% by weight, preferably from 42.5 to

65% by weight, even more preferably 45 to 62.5% by weight, and most preferably from 47.5 to 60% by weight.

- Preferred synthetic rubbers for use in the present invention are EPM and
- 5 EPDM. They are ethylene-propylene copolymer and ethylene-propylene-diene terpolymer, respectively, of which the Mooney viscosity (ML1+4 100°C) is 30 or more and the propylene content is 35% or more, preferably 40% or more, more preferably 45% or more. Although neither the Mooney viscosity nor the propylene content has its respective upper limits, generally available EPM and
- 10 EPDM have a Mooney viscosity (ML 1+4 100°C) of about 20-150 and a propylene content of about 20-50%. However, in the masterbatches of the present invention EP(D)M having a higher Mooney viscosity and/or higher propylene content can be used as well. Other preferred elastomers for use according to the present invention are ethylene-vinyl acetate copolymer, and
- 15 ethylene octene copolymers (POE's), such as Engage® ex Dupont Dow Elastomers. Preferably the POE has a high octene content.

- In the masterbatches of the present invention use may be made of any silica fulfilling the specific surface area and/or pore volume criteria. Wet-treated silica,
- 20 being silica that is precipitated from an aqueous phase, which includes essentially all conventional precipitated silicas as well as silicates, and dry-treated silica, being silica that is pyrogenic in nature. Examples of wet-treated silica are NipsilNS-P™, NipsilVN-3™, NipsilNS-K™ (made by Nihon Silica), MizukasilP-802™, MizukasilP-554A™ (made by Mizusawa Chem. Ind.),
- 25 FinesilE50™, FinesilT32™, FindsilX37™, FinesilX80™, FinesilK41™ (made by Tokuyama), Sipernat 22™, Sipernat 50S™, Sipernat 50™, FK500LS™, FK700™ (made by Degussa), Ketjensil SM660™, Ketjensil SM614™, Ketjensil SM611™ (made by Akzo-PQ), Hi-Sil132™, and Hi-Sil135™ (made by PPG). Examples of dry-treated silica are Aerosil200™, Aerosil300™, Aerosil380™
- 30 (made by Nihon Aerosil). The most preferred silica for use in the invention has a specific surface area of 200 m²/g or more.

Preferred porous silicas (silica gel) have a pore volume of 1.5 ml/g or more,

- such as Mizukasil P-707™, Mizukasil P-740™, Mizukasil P-78F™, Mizukasil P-78D™, Mizukasorb C-I™, Mizukasorb C-6™ (made by Mizusawa Chem. Ind.), Silicia 250™, Silicia250N™, Silicia 256™, Silicia 256N™, Silicia 310™, Silicia 320™, Silicia 350™, Silicia 358™ (made by Fuji Silicia). The (porous) silica is generally used in a powdery state, the preferable average particle size being about 1-15 µm.
- Also silica that has been treated to make it more hydrophobic, e.g. by means of a treatment with methylchlorosilane, can be used, provided it has the specific surface area and/or pore volume. One specific kind or type of silica can be used. However, also mixtures of various silicas are suitable, as long as the final mixture of silicas has the required specific surface area and/or pore volume.
- The specific surface area and the pore volume of the silica are determined in a conventional way by measuring the N₂ isothermal absorption line in accordance with the BET method (as in DIN 66131).
- Wet-treated silica has small holes due to the agglomeration of particles. In the determination of the pore volume both these holes between the particles and the pores of the silica are analyzed. It was found that, irrespective of the true pore volume, any wet-treated silica is suitable as long as the BET analysis shows a pore volume of at least 1.4 ml/g, more preferably of at least 1.5 ml/g.
- Although the present invention imposes no upper limit on the specific surface area and the pore volume of the silica, a practical limit may be found in the commonly available silicas. At present, a practical upper limit for the specific surface area and the pore volume appears to be about 700 m²/g and about 1.8 ml/g, respectively. However, if available, also silicas having a higher specific surface area, e.g. up to 1,000 m²/g, and a higher pore volume, e.g. up to 2.0 ml/g, can be used.
- In order to be able to make masterbatches with the highest possible organic peroxide concentration, the specific surface area and pore volume should be as high as possible. Therefore, it is preferred to use silicas with a specific surface area of at least 200 m²/g and/or a pore volume of at least 1.5 ml/g, preferably

at least 1.6 ml/g.

- The high-concentration cross-linking masterbatch of the present invention containing organic peroxide, synthetic rubber, and silica may additionally
- 5 contain one or more conventional inorganic fillers (as commonly used in the elastomer processing process), as long as these fillers do not adversely affect the performance and storage stability of the masterbatch. Preferred inorganic fillers are precipitated calcium carbonate, heavy calcium carbonate, talc, clay, and carbon black. Their surfaces may be treated with fatty acid, silane-type
- 10 coupling agent, and other compounds.

The masterbatches of the present invention may further contain one or more adjuvants selected from the group of antioxidants, UV stabilizers, flame retardants, pigments, dyes, processing oils, lubricants, and other additives that

15 are commonly used in elastomers. These products are to be used in the conventional amounts, provided that they do not adversely affect the performance and storage stability of the masterbatch. Typically, they constitute 5% by weight or less of the total masterbatch.

- 20 The cross-linking masterbatch of the present invention may be produced by mixing the above ingredients in any suitable way. Typically, use is made of an open roll mill, a Banbury mixer, a kneader, an extruder, or a transfer mixer, which equipment is commonly used for elastomer processing. The preferred mixer is an open roll mill. In order to produce sheets or granules of the
- 25 masterbatch of the present invention, a pelletizer, a cutter, and similar equipment can be added to the mixer.

The masterbatch of the present invention is suitable for use in cross-linking a cross-linkable elastomer. Examples of preferable elastomers to cross-link are

30 EPM, EPDM, ethylene-vinyl acetate copolymer, natural rubber, polybutadiene, polyisoprene, polybutylene, polyisobutylene, polyacrylic acid ester, styrene-butadiene copolymer, acrylonitrile-butadiene copolymer, hydrogenated

acrylonitrile-butadiene copolymer, acrylonitrile-butadiene-styrene terpolymer, fluorinated rubber, silicone rubber, urethane rubber, polyethylene, ethylene- α -olefine copolymer, and chlorinated polyethylene.

- 5 The high-concentration cross-linking masterbatch of the present invention is typically used in amount of by 0.2-20% by weight, preferably 1-10% by weight, relative to the weight of the elastomer to be cross-linked.

Cross-linking of the elastomer may be carried out using any conventional process. In such processes the elastomer to be cross-linked typically is first homogeneously mixed with an inactive filler such as talc and calcium carbonate, a pigment such as carbon black, a processing oil for better processing, etc., and then kneaded with the required amount of the high-concentration cross-linking masterbatch of the present invention. In the subsequent cross-linking step the mixture is typically heated to 140-200°C for 5-30 min in a mould. Depending on the type of elastomer and the types of ingredients used, the cross-linking conditions may vary.

20 EXAMPLES

Example 1

Kayacumyl D (dicumyl peroxide made by Kayaku Akzo, mp (melting point) 38°C, purity 99%) was mixed homogeneously with Nipsil NS-P (specific surface area 170 m²/g), and then kneaded homogeneously with Esprene (EPDM made by Sumitomo Kagaku, Mooney viscosity (ML 1+4 120°C) 80, propylene content 45%) on an open roll mill using the amounts shown in Table 1. Subsequently, the mixed product was cooled and pelletized in a conventional manner, to obtain a granular high-concentration cross-linking masterbatch according to the present invention.

10

Example 2

- Perkadox 14 (m,p-bis(tert-butylperoxyisopropyl) benzene made by Kayaku Akzo, mp (melting point) 43°C, purity 99%) was mixed homogeneously with Sipernat 50S (specific surface area 450 m²/g) and conventional light calcium carbonate, and then kneaded homogeneously with Keltan 312 (EPDM made by Idemitsu DSM, Mooney viscosity(ML 1+4 100°C) 52, propylene content 50%) using an open roll mill and the compounding ratios shown in Table 1. The product was cooled to ambient temperature and cut up into 50X50 cm square sheets (masterbatch) according to the present invention.

10

Example 3

- Kayacumyl D was mixed homogeneously with Aerosil 200 (specific surface area 200 m²/g), surface-treated calcium carbonate (Hakuenka CCR made by Shiroishi Kogyo), and regular polybutene as a processing oil, and then kneaded homogeneously with Mitsui EPT0045 (EPM made by Mitsui Kagaku, Mooney viscosity (ML 1+4 100°C) 38, propylene content 49%) on an open roll mill using the compounding ratios shown in Table 1. The product was cooled to ambient temperature and cut up into 50X50 cm square sheets (masterbatch) according to the present invention.

20

Example 4

- Perkadox 14 was mixed homogeneously with Finesil X80 (specific surface area 250 m²/g) and regular talc and then kneaded homogeneously with JSR-EP11 (EPM made by Nihon Gosei Gum, Mooney viscosity (ML 1+4 100°C) 40, propylene content 49%) using an open roll mill and the compounding ratios shown in Table 1. The product was cooled and pelletized to obtain a granular high-concentration cross-linking masterbatch of the present invention.

- The cross-linking masterbatches of the present invention obtained in Examples 30 1-4 were tested for their storage stability. Their compounding ratios and results are shown in Table 1 and Table 2. In the tables, hardness is a value measured in the conventional way using a Rubber Tester type C, the compounding ratio is

shown as % by weight, and the abbreviations have the following meaning:

- PO: organic peroxide
 KYKD: Kayacumyl D
 PKD: Perkadox 14
 5 MitsuiO045: Mitsui EPT0045
 EP11: JSR-EP11
 ES532: Esprene 532
 KT312: Keltan 312
 NipNSP: Nipsil NS-P
 10 Sipe50S: Sipername 50S
 Fi50S: Finesil 50S
 Aero200: Aerosil 200
 LCC: Light calcium carbonate
 CCR: Hakuenka CCR
 15 PO conc.(%): PO concentration(%) as analyzed in the product

Table 1 Compounding Ratio

	Example 1	Example 2	Example 3	Example 4
PO	KYKD	PKD14	KYKD	PKD14
Ratio(%)	45.1	50.3	55.2	65.0
EMP				
EMDP			Mitsui 0045	EP11
Ratio(%)	ES532 30.0	KT312 25.0		20.0
			25.0	
Wet-treated silica / Dry- treated silica	NipNSP	Sipe50S		Fi50S
Ratio(%)	24.9	18.0	Aero200 15.0	14.0
Filler		LCC	CCR	Talc
Ratio(%)		6.7	3.0	1.0
Additive			Polybutene	
Ratio(%)			1.8	
Shape	Granular	Sheet	Sheet	Granular
PO conc.(%)	44.5	49.8	54.6	64.3
Hardness	60	59	55	59

Table 2 Storage stability test (40°C/after 4 weeks)

	Example 1	Example 2	Example 3	Example 4
Remaining PO(%)	98.8	98.5	98.1	98.7
Appearance	No change	No change	No change	No change
Hardness	60	57	54	60

Example 5

- 5 Trigonox 29 (made by Kayaku Akzo, 1,1-di-tert-butylperoxy-3,3,5-trimethyl cyclohexane, liquid at ambient temperature, purity 95%) was mixed homogeneously with Silicia 250N (pore volume 1.80 ml/g), Hakuenka CCR, and conventional polybutene, and then kneaded homogeneously with Esprene 532 using an open roll mill and the compounding ratios shown in Table 3. The product was cooled to ambient temperature and cut up into 50X50 cm square sheets, to give a high-concentration cross-linking masterbatch of the present invention.
- 10

Example 6

- 15 Trigonox 29 was mixed homogeneously with Mizukasorb C-1 (pore volume 1.70 ml/g) and then kneaded homogeneously with Keltan 312 on an open roll mill, using the compounding ratios shown in Table 3. The product was cooled to ambient temperature and cut up into 50X50 cm square sheets, to give a high-concentration cross-linking masterbatch of the present invention.
- 20

Example 7

- Kayahexa AD (made by Kayaku Akzo, 2,5-dimethyl-2,5-di (tert-butylperoxy) hexane, liquid at ambient temperature, purity 90%) was mixed homogeneously with Mizukasil P-7 (pore volume 1.57 ml/g) and regular talc, and then kneaded
- 25 homogeneously with Mitsui EPT 0045 using an open roll mill and the compounding ratios shown in Table 3. The product was cooled to ambient temperature and pelletized, to give a granular high-concentration cross-linking masterbatch according to the present invention.

Example 8

- Trigonox 17 (made by Kayaku Akzo, 4,4-di-tert-butylperoxyvaleric acid n-butyl ester, liquid at ambient temperature, purity 90%) was mixed homogeneously
5 with Silicia 350 (pore volume 1.60 ml/g) and then kneaded homogeneously with JSR-EP11 on an open roll mill using the compounding ratios shown in Table 3. The product was cooled to ambient temperature and pelletized, to give a granular high-concentration cross-linking masterbatch according to the present invention.

10

The cross-linking masterbatches of the present invention obtained in Examples 5-8 were tested for their storage stability, see Tables 3 and 4. In the tables, the compounding ratio is shown as percentage by weight, and the abbreviations have the following meaning:

- 15 TRN29: Trigonox 29
KYHAD: Kayahexa AD
Si: Silicia
Miso: Mizukasolb
Misi: Mizukasil
20 Porous Si: Porous silica

The other abbreviations have the same meaning as in Table 1.

Table 3 Compounding Ratio

	Example 5	Example 6	Example 7	Example 8
PO Ratio(%)	TRN29 44.4	TRN29 50.0	KYHAD 55.0	TRN17 65.0
EPM EPDM Ratio(%)	ES532 30.0	Kt312 25.0	MitsuiO045 20.0	EP11 20.0
Porous Si Ratio(%)	Si25ON 25.6	MisOC-1 20.0	MisiP-707 19.0	Si350 14.0
Filler Ratio(%)		LCC 5.0	CCR 4.0	Talc 1.0
Additive Ratio(%)			Polybutene 2.0	
Shape	Granular	Sheet	Sheet	Granular
PO conc.(%)	42.0	47.7	51.6	59.2
Hardness	35	37	33	36

Table 4 Storage stability test (40°C/after 4weeks)

	Example 5	Example 6	Example 7	Example 8
Remaining PO (%)	98.7	98.9	98.3	98.6
Appearance	No change	No change	No change	No change
Hardness	36	37	33	38

- 5 Table 2 and Table 4 reveal that the high-concentration cross-linking masterbatch of the present invention loses little organic peroxide and shows almost no change in appearance and hardness over its storage, so that it has excellent storage stability.
- 10 Examples 9-12
- The masterbatches produced in Examples 1-4 were evaluated with respect to their respective cross-linking performances. The prescribed ingredients were mixed at the ratios shown in Table 5. A Banbury mixer was used to obtain the EPDM compound into which each the masterbatches of Examples 1-4 was dispersed at the given ratio using a two-roll mill.
- 15

The amount of masterbatch dispersed into the EPDM compound was chosen such that 0.185 g of active oxygen (from the organic peroxide) was added per 100 g of EPDM.

Table 5 shows the time required to disperse each of the corresponding masterbatches into the EPDM compound.

- 5 Each of the elastomer compositions was cross-linked at 180°C for 15 min.

The cross-linking property of each the treated elastomer compositions was measured by a culastometer (type JSR3). T_{10} and T_{90} stand for the time to reach 10% and 90% of maximum torque, respectively.

10

The cross-linked elastomer was subject to a tensile strength test and a tearing strength test based on JISK-6301. T_b and E_b mean tension and elongation at break, respectively. H_s and TR mean hardness and resistant strength against tearing of a cross-linked elastomer, respectively.

15

Table 5 shows compounding ratios of ingredients and test results. In the table, JSR-EP86 is the trade name for EPDM made by Nihon Gosei Gum KK. Asahi carbon #70 and Sunpar 2280 made by Nihon Sun Sekiyu KK were used as HAF carbon black and naphthenic processing oil, respectively. A phenolic ageing protector was used. The abbreviations have the following meaning:

TMPT: trimethylolpropane trimethacrylate

JSREP86: JSR-EP86

HAF-C: HAF carbon black

NP oil: naphthenic processing oil

25 A: The masterbatch produced in Example 1

B: The masterbatch produced in Example 2

C: The masterbatch produced in Example 3

D: The masterbatch produced in Example 4

"A 7.2" in the masterbatch row of the table means that 7.2 parts of the

30 masterbatch produced in Example 1 were used. The other masterbatch abbreviations have corresponding meanings.

Table 5 Elastomer compositions (parts by weight) and results

	Example 9	Example 10	Example 11	Example 12
JSREP86	100	100	100	100
HAF-C	50	50	50	50
NP oil	10	10	10	10
Ageing protector	2	2	2	2
TMPT	2	2	2	2
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
Masterbatch	A 7.2	B 4.0	C 5.9	D 3.1
Disperse time (min)	3.5	3.1	2.2	2.5
Cross-linking property	T ₁₀ (min)	1.3	1.0	1.3
	T ₉₀ (min)	8.8	8.2	8.9
	Max torque (kgf/cm)	34	36	35
Tensile strength test	T _B (kgf/cm ²)	180	174	177
	E _B (%)	450	410	430
	H _s (JIS-A)	71	71	71
Tearing test	TR (kgf/cm)	43	41	43

Examples 13-16

- 5 The cross-linking properties of the masterbatches produced in Examples 13-16 were evaluated in the same way as was done in Examples 5-8, except that the cross-linking conditions were 150°C for 15 min in Examples 13 and 14, 180°C for 15 min in Example 15, and 160°C for 15 min in Example 16.
- 10 The results are compiled in Table 6.
- The following abbreviations were used:
- E: The masterbatch produced in Example 5
 - F: The masterbatch produced in Example 6
 - G: The masterbatch produced in Example 7
 - 15 H: The masterbatch produced in Example 8

Table 6 Elastomer compositions (parts by weight) and results

	Example 13	Example 14	Example 15	Example 16
JSREP86	100	100	100	100
HAF-C	50	50	50	50
NP oil	10	10	10	10
Ageing protector	2	2	2	2
TMPT	2	2	2	2
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
Masterbatch	E 8.2	F 7.3	G 6.3	H 6.2
Disperse time (min)	2.8	1.5	1.0	1.2
Cross-linking property	T ₁₀ (min)	0.8	0.8	1.4
	T ₉₀ (min)	5.1	5.2	8.9
Max torque (kgf/cm)	13	13	30	13
Tensile strength test	T _B (kgf/cm ²)	182	183	177
	E _B (%)	350	340	330
	Hs (JIS-A)	63	63	68
Tearing test	TR (kgf/cm)	42	42	40
				41

- 5 Table 5 and Table 6 show that the cross-linking masterbatches of the present invention can be readily dispersed into an elastomer and that their use results in cross-linked products having excellent properties such as mechanical strength, i.e. tensile strength and resistance against tearing.
- 10 Clearly, the present invention provides effective, highly concentrated organic peroxide masterbatches having excellent storage stability.

CLAIMS

1. A concentrated cross-linking masterbatch comprising one or more organic peroxides, one or more synthetic rubbers, and silica, wherein said organic peroxide constitutes from 40 to 70% by weight, based on the total weight of the masterbatch, and said silica has a specific surface area of 150 m²/g or more or a pore volume of 1.4 ml/g or more.
5
2. A masterbatch according to claim 1 wherein the silica is characterized by (a) a specific surface area of 150 m²/g or more if said organic peroxide is a solid at ambient temperature, or (b) a pore volume of 1.4 ml/g or more if said organic peroxide is a liquid at ambient temperature.
10
3. A masterbatch according to claim 1 or 2 wherein said synthetic rubber is an ethylene propylene rubber or an ethylene propylene diene rubber which preferably contains at least 45% by weight of propylene and has a Mooney viscosity at 100°C of 30 or more.
15
4. A masterbatch according to any one of claims 1-3 wherein said organic peroxide is present in an amount of from 42.5 to 65% by weight, said synthetic rubber is present in an amount of 10-30% by weight, and said silica is present in an amount of 5-30% by weight, relative to the total masterbatch weight.
20
- 25 5. A masterbatch according to any one of the preceding claims further comprising one or more inorganic fillers, preferably selected from the group of calcium carbonate, heavy calcium carbonate, talc, clay, and carbon black.
- 30 6. A masterbatch according to any one of the preceding claims further comprising one or more adjuvants selected from the group of antioxidants, UV stabilizers, flame retardants, pigments, dyes, processing oils, and lubricants, which preferably are present in an amount of less than 5% by

weight, based on the weight of the total masterbatch.

7. Use of a masterbatch according to any one of claims 1-6 in the process of vulcanizing an elastomer.

INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/EP 00/06246

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08K5/14 C08K3/22 C08J3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08K C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 09, 31 October 1995 (1995-10-31) -& JP 07 165990 A (KAYAKU AKZO KK), 27 June 1995 (1995-06-27) table 1 ---	1,2,7
A	EP 0 708 132 A (PEROXID CHEMIE GMBH) 24 April 1996 (1996-04-24)	1,3,5,7
X	page 3, line 29 - line 33; claims 1,5,9 -----	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

25 October 2000

Date of mailing of the international search report

03/11/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Engel, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/06246

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
JP 07165990 A	27-06-1995	NONE		
EP 0708132 A	24-04-1996	DE 4437465 A	25-04-1996	US 5589526 A 31-12-1996

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 January 2001 (18.01.2001)

PCT

(10) International Publication Number
WO 01/04200 A1

- (51) International Patent Classification⁷: C08K 5/14. (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).
- (21) International Application Number: PCT/EP00/06246 (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (22) International Filing Date: 3 July 2000 (03.07.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 11/192632 7 July 1999 (07.07.1999) JP (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicants (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). KAYAKU AKZO CORPORATION [JP/JP]; Kojimachi NK Building, 14-2, Kojimachi, 2-chome, Chiyoda-ku, Tokyo 102 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): ISHIDO, Akio [JP/JP]; 7-6 Minatomati, Onoda-shi, Yamaguchi-ken (JP). TAKAI, Akihiko [JP/JP]; 1401-10 Oazanishikiha, Ube-shi, Yamaguchi-ken (JP).

Published:

- With international search report.
- With amended claims.

Date of publication of the amended claims: 15 March 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/04200 A1

(54) Title: HIGH-CONCENTRATION CROSS-LINKING MASTERBATCHES

(57) Abstract: The invention relates to a cross-linking masterbatch comprising more than 40 % by weight of organic peroxide, a synthetic rubber, and a specific silica. More specifically, a highly concentrated cross-linking masterbatch is provided comprising from 40 to 70 % organic peroxide, a synthetic rubber such as EPM and/or EPDM, preferably having a propylene content of 45 % or more and a Mooney viscosity at 100 °C of 30 or more, and a wet-treated and/or dry-treated silica having a specific surface area of 150 m²/g or more or a porous silica having a pore volume of 1.4 ml/g or more.

AMENDED CLAIMS

[received by the International Bureau on 3 January 2001 (03.01.01);
original claim 1 amended; remaining claims unchanged (2 pages)]

1. A concentrated cross-linking masterbatch comprising one or more organic peroxides, one or more synthetic rubbers, and silica, wherein said organic peroxide constitutes from 40 to 70% by weight, based on the total weight of the masterbatch, and said silica has a specific surface area of 150 m²/g or more or a pore volume of 1.4 ml/g or more, with the proviso that the masterbatch does not comprise a trans-polyoctenamer.
- 10 2. A masterbatch according to claim 1 wherein the silica is characterized by (a) a specific surface area of 150 m²/g or more if said organic peroxide is a solid at ambient temperature, or (b) a pore volume of 1.4 ml/g or more if said organic peroxide is a liquid at ambient temperature.
- 15 3. A masterbatch according to claim 1 or 2 wherein said synthetic rubber is an ethylene propylene rubber or an ethylene propylene diene rubber which preferably contains at least 45% by weight of propylene and has a Mooney viscosity at 100°C of 30 or more.
- 20 4. A masterbatch according to any one of claims 1-3 wherein said organic peroxide is present in an amount of from 42.5 to 65% by weight, said synthetic rubber is present in an amount of 10-30% by weight, and said silica is present in an amount of 5-30% by weight, relative to the total masterbatch weight.
- 25 5. A masterbatch according to any one of the preceding claims further comprising one or more inorganic fillers, preferably selected from the group of calcium carbonate, heavy calcium carbonate, talc, clay, and carbon black.
- 30 6. A masterbatch according to any one of the preceding claims further comprising one or more adjuvants selected from the group of antioxidants, UV stabilizers, flame retardants, pigments, dyes, processing oils, and

lubricants, which preferably are present in an amount of less than 5% by weight, based on the weight of the total masterbatch.

7. Use of a masterbatch according to any one of claims 1-6 in the process of vulcanizing an elastomer.